A METHOD FOR PREPARING LITHIUM MANGANESE SPINEL OXIDE HAVING IMPROVED ELECTROCHEMICAL PERFORMANCE

BACKGROUND OF THE INVENTION

(a) Field of the Invention

5   The present invention relates to a method for preparing lithium manganese complex oxide, $Li_{1+x}Mn_{2-x}O_4$ (0 x 0.12), with a spinel structure used for a cathode active material of a lithium or lithium ion secondary battery.

(b) Description of the Related Art

10      $LiCoO_2$ compound is most commonly used for a cathode active material of a lithium or lithium ion secondary battery having an electric potential of 4 V (voltage).   However, many studies for other active materials have been conducted recently, because $LiCoO_2$ compound is expensive and disadvantageous in terms of stability.   A lithium manganese complex oxide, 15 $Li_{1+x}Mn_{2-x}O_4$ (0 $\leq$ x $\leq$ 0.12), with a spinel structure, is one of the most actively studied materials, because it is inexpensive and stable during its usage, and it has an environmental affinity.

The conventional method for synthesizing lithium manganese complex oxide with a spinel structure comprises mixing a manganese 20 compound and a lithium compound so as to adjust their chemical compositions, and heat-treating the mixture at a high temperature.   USP 5,718,877 discloses a heat-treatment process for obtaining chemically uniform spinel, and R. J. Gummow et al., Solid State Ionics, 69, 59(1994) state that a compound with a spinel structure is not limited to the 25 stoichiometry of $LiMn_2O_4$, and a spinel structure forms even if x in $Li_{1+x}Mn_{2-x}O_4$ varies from 0 to 0.33, and, as x increases, the valence of Mn reaches 4 and the crystalline structure becomes stabilized.

After it was reported that the deterioration of electrochemical

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characteristics of lithium manganese complex compound with a spinel structure is promoted by nonuniformity of spinel composition, various studies for synthesizing more chemically uniform spinel using a liquid phase method have been attempted.   However, with most liquid phase methods, a spinel

5   compound having a particle size of several μm or less is obtained.   Such micro particles are difficult to use as a cathode active material of a battery, because they have poor particle flow characteristics, charge density, tap density, and wettability for solvent, and thus they have many problems in the electrode preparation process, even if each particle has excellent

10   electrochemical properties.

Recently, it was found that defects in raw materials, particularly electrolytic manganese dioxide (EMD), promote nonuniformity of the composition or local defects of structure when synthesizing spinel, and deteriorate the electrochemical properties of spinel.   Inside EMD, a raw

15   material of manganese, a variety of defects introduced during the process of synthesis (impurities, absorbed water, crystalline water, hydrogen ions, and other ions such as SO_4^{2-}, Cl, NH^{4+}, etc.) exist.   Such impurities form a stable mesophase that exists as impurities during the heat-treatment process for obtaining the spinel compound of $Li_{1+x}Mn_{2-x}O_4$.   In addition, such defects

20   may deteriorate performance when used as a cathode active material of a lithium or lithium ion secondary battery, because the synthesized compound has internal lattice defects, even if it has a spinel structure.   Specifically, lithium diffuses into a lattice of a spinel compound when charging/discharging, and the partial lattice defects inhibit the movement of

25   lithium in the process of insertion and deintercalation, as well as react with lithium to decrease the amount of movable lithium, and consequently decreases the capacity of the battery.

There have been many attempts at removing the above-mentioned defects.   The most representative method is acid treating or base treating

30   the raw material powder in a strong acid or a strong base.   The acid

treatment method is used to remove impurity metal ions existing in the raw material, and the base treatment method is used to substitute hydrogen ions in the raw material with lithium. Since these methods are used with aqueous solutions, they involve the risk of moisture infiltration into the raw
5   material and the absorbed water may be incorporated therein. In addition, since particles strongly aggregate after they are dried of the aqueous solution, the above methods involve a pulverizing process, during which process the impurities may be incorporated again, and they have the inconvenience that an acid treatment cannot be conducted simultaneously
10   with a base treatment to remove the impurities.

Another inherent problem is the shape of the secondary aggregate of the manganese raw material. When the mixture of manganese dioxide and lithium compound is heat-treated, lithium infiltrates the manganese compound and a reaction proceeds, and the shape of the formed spinel
15   nearly maintains the shape of the particle of manganese raw material. Therefore, in order to control the shape of the spinel particle, the shape of the particle of manganese dioxide should be controlled.

SUMMARY OF THE INVENTION

20   It is an object of the present invention to provide a method of preparing a manganese compound having an improved secondary aggregate shape without defects existing in the particles of the manganese compound raw material, in order to obtain a lithium manganese complex oxide with a spinel structure having improved performance, considering the
25   above-mentioned problems of the prior art.

It is another object of the present invention to provide a method of preparing a lithium manganese spinel having improved performance using a manganese compound prepared according to the above method, which has improved particle shape and which does not have internal defects, as the
30   manganese raw material.

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It is another object of the present invention to provide a lithium or lithium ion secondary battery having improved electrochemical characteristics using a lithium manganese complex oxide with a spinel structure having improved performance, prepared according to the above

5   method, that is obtained from the manganese compound that has improved particle shape and which does not have internal defects, as a cathode active material.

In order to achieve these objects, the present invention provides a method of preparing a manganese compound that is a raw material for a

10 lithium manganese complex oxide, comprising the step of simultaneously applying a mechanical force and a heat energy to a manganese compound to remove defects present in particles of said manganese compound, and to control the aggregation of particles and the shape of the aggregated particles.

The present invention also provides a method of preparing lithium

15 manganese complex oxide with a spinel structure, comprising the steps of (a) mixing (i) a manganese compound prepared according to the method comprising the step of simultaneously applying a mechanical force and a heat energy to remove defects present inside particles of a manganese compound and to control the aggregation of particles and the shape of the

20 aggregated particles, and (ii) a lithium compound; and (b) calcinating the mixture obtained in said step (a).

The present invention also provides a lithium or lithium ion secondary battery comprising a lithium anode, an electrolyte and a cathode using lithium manganese complex oxide powder with a spinel structure as an

25 active material, wherein said cathode active material is lithium manganese complex oxide with a spinel structure that is prepared by the method comprising the steps of (a) mixing (i) a manganese compound prepared according to the method comprising the step of simultaneously applying a mechanical force and a heat energy to remove defects present inside

30 particles of said manganese compound and to control the aggregation of

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particles and the shape of the aggregated particles, and (ii) a lithium compound; and (b) calcinating the mixture obtained in said step (a).

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the result of analyzing the distribution of defects present in the particles of MH-treated manganese dioxide using a thermal weight analyzer, according to the amount of time of MH treatment.

Figure 2 shows the change of the average valence of Mn in MH-treated manganese dioxide raw material, according to the amount of time of MH treatment.

Figure 3 shows a scanning electron microscope (SEM) photograph enlarged 500-fold expressing the shape of particles of manganese dioxide before MH treatment.

Figure 4 shows a scanning electron microscope (SEM) photograph enlarged 500-fold expressing the shape of particles of manganese dioxide after MH treatment.

Figure 5 shows the size of manganese dioxide particles before and after MH treatment and the distribution thereof.

Figure 6 shows the true density of lithium manganese spinel synthesized using MH-treated raw material, according to the amount of time of MH treatment.

Figure 7 shows the tap density of lithium manganese spinel synthesized using the MH-treated raw material of Example 1 and Example 2, according to the amount of time of MH treatment.

Figure 8 shows the charge/discharge characteristics of batteries of Example 1, Example 2 and Comparative Example.

Figure 9 shows the life characteristics of batteries of Example 1, Example 2 and Comparative Example.

Figure 10 shows a typical mechanofusion mill, wherein reference numeral 1 indicates a mixing chamber, 2 indicates a chamber wall, 3 indicates a fixing axis, 4 indicates the direction of chamber rotation, 5

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indicates a thermoelectric zone, 6 indicates a scraper and 7 indicates an external heater.

DETAILED DESCRIPTION AND THE PREFERRED EMBODIMENTS

The present invention prepares a manganese compound that is a
5   raw material for a lithium manganese complex oxide by applying a mechanical force and a heat energy to remove defects present inside particles of the manganese compound, prepares a lithium manganese complex oxide with a spinel structure using said manganese compound, and provides a lithium or lithium ion secondary battery using said lithium
10   manganese complex oxide with a spinel structure as a cathode active material.

In the present invention, the operation of applying mechanical force and heat energy is referred to as "MH treatment". The mechanical force is applied to a particle of manganese compound raw material, and it produces
15   strain in the aggregated particle to increase driving force that can rearrange the atoms according to their movement. Simultaneously, heat is applied to promote the rearrangement and evaporate absorbed water, water of crystallization, hydrogen ions and other evaporable ions present inside the secondary particles of the raw material.

20   Such MH treatment may decrease the concentration of defects present in the particles of the manganese compound, thereby increasing the average valence of Mn therein.

The results of MH treatment are proved by the following explanations of the drawings.

25   Figure 1 shows the results of analyzing the defects in the particles before and after MH treatment using a thermal gravimetry analyzer, indicating that the total defects largely decrease after MH treatment compared to those before MH treatment.

Figure 2 shows the average valence of the Mn according to the
30   amount of time of MH treatment, and indicates that, as the amount of time of

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MH treatment increases, the valence increases.   This is because the volatile ions that exist as impurities such as NH^{4+}, H^3O+, etc. are discharged to increase the valence of Mn.

Figures 3 and 4 show the shapes of manganese dioxide particles before and after MH treatment, respectively, as seen through a SEM, indicating that the shape drastically changes.

Figure 5 shows the result of analyzing the size of manganese dioxide particles before and after MH treatment and the distributions thereof using a grading analyzer, indicating that after MH treatment, the size of manganese dioxide secondary particles is suitable for use as a cathode active material.

Such MH treatment of the present invention can be conducted using a specific apparatus that can apply shear stress to the surface of particles, such as a ball mill, attrition mill, jet mill, centrifugal mill, etc., to which a heating apparatus is attached.   Such shear stress applies stress to particles to increase a driving force for the movement of atoms in the material, and simultaneously, a heat energy evaporates volatile impurities while promoting the movement of material.

A preferable example of said apparatus is surface coating apparatus called "a mechanofusion mill" as used in the Example of the present invention.   Said apparatus has the advantage of being capable of applying mechanical force such as shear stress, compression stress, etc. to a particle and externally controlling the temperature, and it is generally used for coating fine metal on ceramic powder.   The principle of the operation of said apparatus is shown in Fig. 10.   Specifically, the manganese compound raw material, is introduced into the mixing chamber (1), and the manganese compound gathers along the rotating chamber wall (2) by centrifugal force and receives shear stress and compression stress at the fixing axis (3). The scraper (6) scrapes the manganese compound attached to the chamber wall (2), and the thermoelectric zone (5) controls heating of the outer heater (7).

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In the present invention, manganese dioxide such as electrolytic manganese dioxide (EMD; MnO_2) and chemical manganese dioxide (CMD; MnO_2), Mn_2O_3 and Mn_3O_4 can be used as the raw material.

The mechanical force applied to said manganese compound is
5 preferably approximately 0.1 to 1000 dyne/cm2, in which range the three-dimensional destruction of the aggregated particles does not occur. Since mechanical energy removes edge parts of the raw material to make it globular, when preparing an electrode from lithium manganese spinel complex oxide that is prepared using a MH-treated manganese compound
10 as a raw material, the surface friction between particles decreases and the true density can be improved. The amount of time of applying mechanical energy and heat energy is preferably 5 minutes to 5 hours. If the time exceeds 5 hours, the particle shape of the prepared manganese compound becomes more spherical, but the disadvantages in terms of operating cost
15 and time are too high. If the time is less than 5 minutes, it is difficult to sufficiently remove defects. The temperature range of heat energy is preferably 50 to 200 ℃.

In said MH-treatment, preparations that make the treatment easy can be added. Preferable preparations include a lithium salt such as LiOH,
20 LiOH· H_2O, $LiCH_3COO$, $LiCHO_2$, $LiCHO_2$· H_2O, $LiNO_3$, and $Mn(CH_3CO_2)_2$, $Mn(NO_3)_2$ having a melting point of less than 200℃, and mixtures of other metal compounds and the above compounds. The amount of the preparations is preferably 0 to 20 wt% of the treated manganese compound.

In addition, in a method of preparing lithium manganese complex oxide
25 $Li_{1+x}Mn_{2-x}O_4$ (0 x 0.12) with a spinel structure comprising the steps of mixing lithium compound and said manganese compound and calcinating the mixture, said lithium compound is preferably selected from a lithium salt group consisting of LiOH, , LiOH· H_2O, $LiCH_3COO$, $LiCHO_2$, $LiCHO_2$· H_2O and $LiNO_3$. In addition, the temperature of calcination is 400 to 900 ℃, and
30 the time of calcinations is 1 to 30 hours.

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The lithium manganese complex oxide with a spinel structure of the present invention is applied to a cathode active material of a lithium battery or lithium ion battery by mixing lithium manganese spinel compound powder in n-methyl pyrrolidine (NMP) solvent using graphite as a conductor and

5 polyvinylidenedifluoride (PVDF) as a binder to prepare a slurry, coating said slurry on aluminum foil by a casting method, drying said slurry to prepare a cathode, and applying said cathode to a lithium secondary battery together with an anode and an electrolyte. Thus obtained battery has much better charge/discharge characteristics and life characteristics than a battery using

10 a lithium manganese spinel compound prepared from the non MH-treated manganese compound of the prior art as a cathode active material.

The present invention will be explained in more detail with reference to the following Examples and Comparative Examples. However, the Examples are to illustrate the present invention, and the present invention is

15 not limited to them.

[Example]

Example 1

MH treatment of manganese compound raw material

In order to remove defects present in electrolytic manganese dioxide

20 (EMD; MnO_2), EMD was MH-treated. Specifically, the weight of MnO_2 raw material was quantified, and the quantified amount of MnO_2 was introduced into a mechanofusion mixer (Japan Kosokawa Company product AM-15) shown in Fig. 10, and shear stress and compression stress were applied to the particles of the raw material while applying 100℃ of heat thereby

25 preparing the modified manganese dioxide.

The change of the distribution of defects present in the particles of MH-treated manganese dioxide (surface absorption, volatile ions, crystalline water, or structural defects) according to the amount of time of MH treatment is shown in Fig. 1.

30 In addition, the change of the average valence of the Mn according to

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the amount of time of MH treatment is shown in Fig. 2.

In addition, SEM photographs of the shapes of the particles before and after MH treatment are shown in Figs. 3 and 4, and the size of the particles and the distribution of the size analyzed by particle size analyzer are shown

5   in Fig. 5.

The preparation of lithium manganese complex oxide with a spinel structure

The prepared MH-treated manganese dioxide raw material was mixed with lithium hydroxide monohydrate (LiOH · H_2O) while controlling the ratio of

10   Mn/Li to 0.538.

The sufficiently mixed powder was heat-treated in a furnace at 400 to 500 ℃ under an air atmosphere for 7 hours.

The heat-treated powder was cooled and then mixed again in order to make the chemical composition uniform.

15   Thus obtained powder was secondarily heat treated in a furnace at 750℃ under an air atmosphere to synthesize lithium manganese spinel powder.

The change of the true density of manganese dioxide in the prepared spinel powder according to the amount of time of MH treatment is shown in

20   Fig. 6, and the change of the tap density of manganese dioxide according to the time of MH treatment is shown in Fig. 7.

The application as a cathode active material and the evaluation of the battery characteristics

The prepared lithium manganese spinel compound powder was used as

25   a cathode active material to prepare an electrode.   Graphite was used as a conductor and polyvinylidenedifluoride (PVDF) was used as a binder.   The weight ratio of the active material, conductor and binder was 85:10:5.

A binder was dissolved in n-methyl pyrrolidinone (NMP) and then an active material and a conductor were added to prepare a slurry.

30   The prepared slurry was coated on aluminum foil by a tape casting

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method, and then it was dried in a vacuum drier at 130 ℃ for 2 hours to prepare a cathode.

Lithium metal was used as an anode. The cathode and the anode were cut to an appropriate size, and then a lithium ion secondary battery was constructed as a coin cell. 1 mole of $LiPF_6$ solution was used as an electrolyte, and the mixed solution of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) in the ratio of 1:2 was used as an electrolytic liquid.

The prepared cell was represented by [$LiMnO_2$/$LiPF_6B$(1M) in EC + 2EMC/Li]. The charge/discharge characteristics and the life characteristics of the cell were evaluated. The evaluation of the capacity was conducted at the range of the charge/discharge voltage of 3.0 to 4.5 V, and the evaluation of the life characteristics was conducted at the range of 3.4 to 4.3 V.

The charge/discharge characteristics are shown in Fig. 8, and the life characteristics are shown in Fig. 9.

Example 2

MH treatment of manganese compound raw material

EMD was MH treated by the same method as described in Example 1, except that 0.03 mole of LiOH · H_2O per 1 mole of MnO_2 was further added as a preparation to enhance MH treatment.

The preparation of lithium manganese complex oxide with a spinel structure

Lithium manganese spinel was prepared by the same method as described in Example 1, except that MH-treated EDM to which said preparation was added was used.

The change of tap density of manganese dioxide in the prepared spinel powder according to the time of MH treatment is shown in Fig. 7.

The application as a cathode active material and the evaluation of the battery characteristics

A battery was prepared by the same method as described in Example 1,

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except that lithium manganese spinel prepared in the above was used as a cathode active material, and the characteristics thereof were evaluated.

The charge/discharge characteristics are shown in Fig. 8, and the life characteristics are shown in Fig. 9.

5 Comparative Example

The preparation of lithium manganese complex oxide with a spinel structure

A lithium manganese spinel was prepared by the same method as described in Example 1, except that manganese raw material that was not

10 MH-treated was used.

The application as a cathode active material and the evaluation of the characteristics of the battery

A battery was prepared by the same method as described in Example 1, except that lithium manganese spinel prepared in the above was used as a

15 cathode active material, and the characteristics of the battery were evaluated.

The charge/discharge characteristics are shown in Fig. 8, and the cyclic performance are shown in Fig. 9.

The lithium or lithium ion secondary battery using lithium manganese complex oxide with a spinel structure without defects of the present invention

20 has excellent charge/discharge characteristics and cyclic performance.